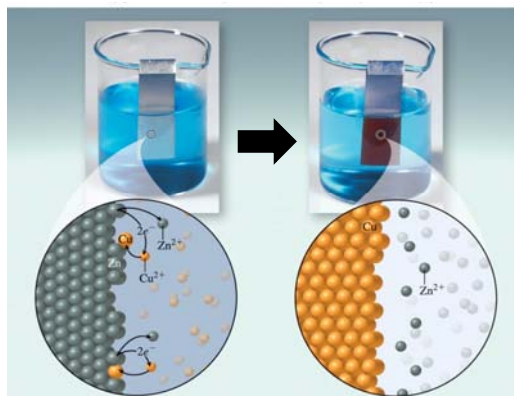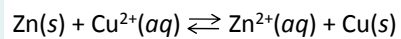# Chapter 19

Electrochemistry

Part I

Electrochemistry

▪ What is *electrochemistry*?

It is a branch of chemistry that studies chemical reactions "*called redox reactions*" which involve *electron transfer*.

Oxidation of zinc in a solution of copper sulfate is an example of oxidation-reduction "***redox***" reactions.

$$Zn(s) + Cu^{2+}(aq) \rightleftarrows Zn^{2+}(aq) + Cu(s)$$

| 0 | +2 | +2 | 0 |

Oxidation states

19.1

Assigning Oxidation States in Redox Reactions

⇨ $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

        0   0   +1   −1

⇨ $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

   −4   +1×4   **0**   +4   −2×2   +1×2   **− 2**

     $CH_4 \longrightarrow CO_2 + 8e^-$ *CH_4 is a reducing agent*

     −4   +4

     $2O_2 + 8e^- \longrightarrow CO_2 + 2H_2O$ *O_2 is an oxidizing agent*

     0   −2×2   −2

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Balancing Redox Reactions in
Acidic Media

$H^+(aq) + Cr_2O_7^{2-}(aq) + C_2H_5OH(l) \longrightarrow Cr^{3+}(aq) + CO_2(g) + H_2O(l)$

Step 1: Write half equations (oxidation-reduction).

     $Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$ (*reduction*)

      +6   +3

     $C_2H_5OH(l) \longrightarrow CO_2(g)$ (*oxidation*)

      -2   +4

Notice that we didn't deal with H^+ and H_2O because they are going to be added at a later stage to balance the redox reaction.
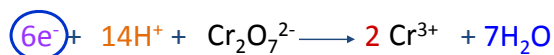
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19.1

Balancing Redox Reactions in
Acidic Media
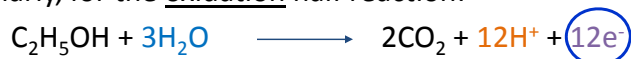
Step 2: Balance all elements and charges for each half reaction.

For the reduction half reaction:

$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2\ Cr^{3+} + 7H_2O$

a) Balance all elements except oxygen and hydrogen atoms.
b) Balance oxygen with H_2O.
c) Balance hydrogen with H^+.
d) Balance charges using electrons.

$+14 - 2 \rightarrow +6$

Similarly, for the oxidation half reaction:

$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 12H^+ + 12e^-$

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19.1

Balancing Redox Reactions in
Acidic Media

Step 3: Equalize the number of electrons in both balanced half reactions.
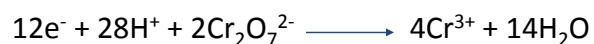
$12e^- + 28H^+ + 2Cr_2O_7^{2-} \longrightarrow 4Cr^{3+} + 14H_2O$ ⬅ The reduction half reaction after being multiplied by 2

Step 4: Add up the two half reactions:

$\cancel{12e^-} + 28H^+ + 2Cr_2O_7^{2-} \longrightarrow 4Cr^{3+} + 14H_2O$
$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 12H^+ + \cancel{12e^-}$

$16H^+ + 2Cr_2O_7^{2-} + C_2H_5OH \longrightarrow 4Cr^{3+} + 11H_2O + 2CO_2$
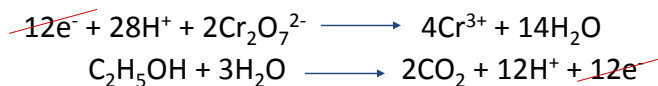
Step 5: Check that elements and charges in the final reaction are balanced.

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Balancing Redox Reactions in
Basic Media

$$Ag(s) + CN^-(aq) + O_2(g) \xrightarrow{\textit{basic}} Ag(CN)_2^-(aq)$$

Step 1: $Ag + CN^- \longrightarrow Ag(CN)_2^-$ (*oxidation*)

$O_2 \longrightarrow$ (*reduction*)

Step 2:

$Ag + 2CN^- \longrightarrow Ag(CN)_2^- + e^-$

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Step 3:

$4Ag + 8CN^- \longrightarrow 4Ag(CN)_2^- + 4e^-$

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$
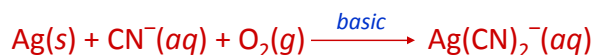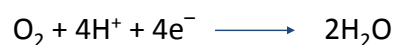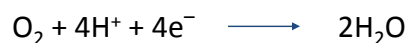
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19.1

Balancing Redox Reactions in
Basic Media

Step 4: $4Ag + 8CN^- + O_2 + 4H^+ \longrightarrow 4Ag(CN)_2^- + 2H_2O$

$+ 4OH^-$ $+ 4OH^-$

Step 5:

$4Ag + 8CN^- + O_2 + \boxed{4H_2O} \longrightarrow 4Ag(CN)_2^- + 2H_2O + 4OH^-$
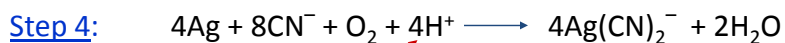
Step 6: Eliminate H_2O molecules from both sides:

$4Ag + 8CN^- + O_2 + 2H_2O \longrightarrow 4Ag(CN)_2^- + 4OH^-$

Step 7: Recheck the balance of elements and charges.

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Galvanic Cells

19.2

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

The two half-reactions can physically be separated in two beakers. As a result, the electrons lost by Zn travel through an external wire in order to be gained by Cu^{2+} ions. *This generates electricity*.

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Galvanic Cells

19.2

- A **galvanic cell** is the experimental apparatus for *generating electricity* through the use of a spontaneous reaction.

Salt bridge

e^- e^-

Anode (−)   Cathode (+)

Aqueous solution   Aqueous solution

Oxidation half-reaction   Reduction half-reaction

Electrodes

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Galvanic Cells

- A *galvanic cell* (also called *voltaic cell*) is the experimental apparatus for *generating electricity* through the use of a spontaneous reaction.

An electric current flows from anode to cathode because there is a difference in electrical potential energy between the two electrodes.

Oxidation   **Electrodes**   **Reduction**

Salt bridge

Oxidation half-reaction   **Reduction half-reaction**
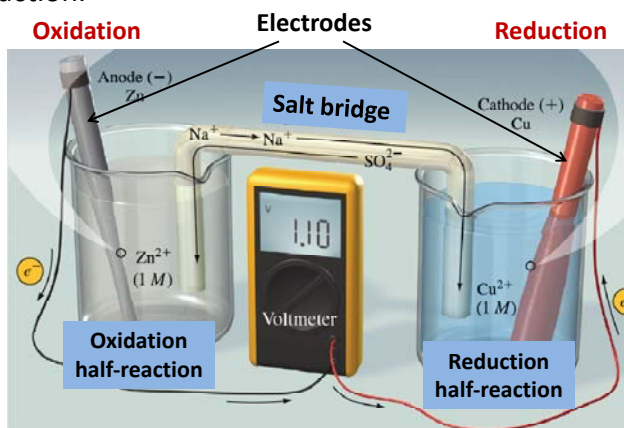
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Salt Bridge

- A *salt bridge* is an essential conducting medium through which the cations and anions can move from one half-cell to the other. It maintains balance of the charge between the two half-cells.

- Ion migration:
  - Cations – migrate toward the cathode
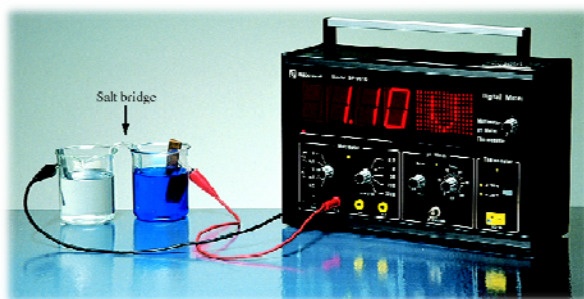 - Anions – migrate toward the anode

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Cell Potential

- The **cell potential** (E_{cell}) is the difference in electrical potential between the anode and cathode half-cells. The cell potential is:
  - o concentration dependent.
  - o temperature dependent.
  - o determined by nature of reactants.

The cell potential is measured using a voltmeter with units of volts (V).

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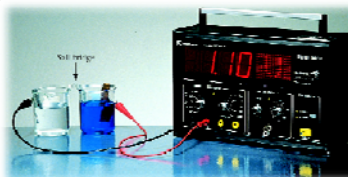

Galvanic Cell Notation

$$\mathrm{Zn}(s) \,|\, \mathrm{Zn^{2+}}\ (1\ M) \,||\, \mathrm{Cu^{2+}}\ (1\ M) \,|\, \mathrm{Cu}(s)$$

Anode ⎯⎯ **Cathode**

Dr. Al-Saadi **Phase boundary** **Salt bridge** **Phase boundary** 14
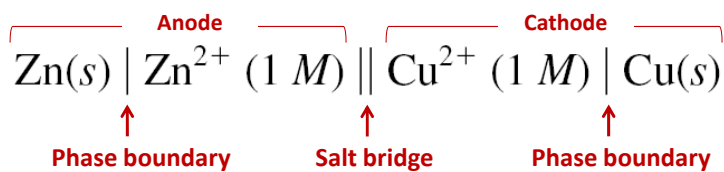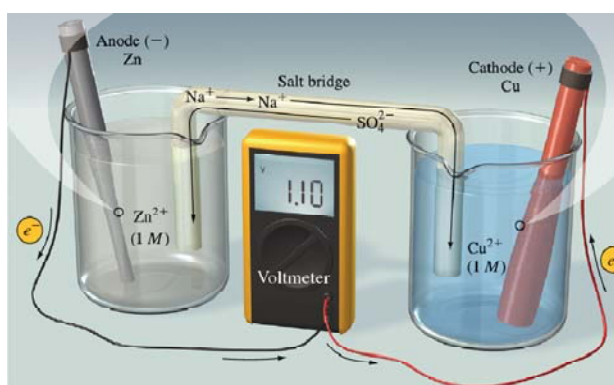

Half-Cell Potential

- Is it possible for the Zn oxidation half-reaction to occur by itself?

  Is it possible for the Cu^{2+} reduction half-reaction to occur by itself?

  The answer is NO.

  A half reaction can not take place independently. Thus, a *half-cell potential* is impossible to be measured. We can only measure a *full-cell potential* that involves anode and cathode half reactions.

- If oxidation (or reduction) of H_2 is taken to be a reference half-reaction and if it is assigned a half-cell potential equal to exactly zero:

$$H_2 \rightarrow 2H^+ + 2e^-$$

Then:

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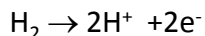
Standard Hydrogen Electrode

Then, the hydrogen electrode is used as a reference for other electrodes.

$$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$$

- The platinum (Pt) electrode is used to:
  - provide a surface on which the oxidation of H_2 can take place.
  - serve as an electrical conductor.

- Under *standard state condition* at 25°C , **the reduction potential** of H^+ is defined as exactly zero.

The standard hydrogen electrode (*SHE*)

$$2H^+ (1\ M) + 2e^- \longrightarrow H_2 (1\ atm) \qquad E° = 0\ V \qquad \textit{By definition}$$

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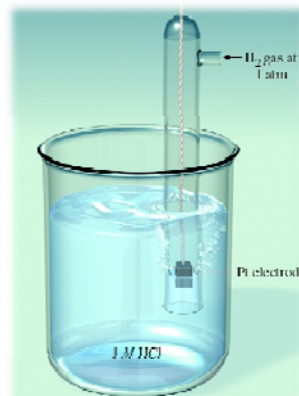
Standard Reduction Potential

- The ***standard reduction potential (E°)*** is the potential associated with a reduction half-reaction at an electrode when the ion concentration is 1 *M* and the gas pressure is 1 atm.

  The standard reduction potential (*E°*) for the hydrogen electrode (SHE) is assigned the value 0 V.

$$E^o_{H^+/H_2} = 0\ V$$ shown as reduction

- The *relative* standard reduction potentials of other half-reactions (all are represented as reduction reactions to avoid unclearness) are measured relative to the SHE potential.
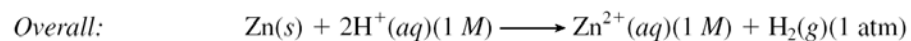
$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

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standard reduction potential for zinc

Measuring $E^o_{Zn^{2+}/Zn}$

$$Zn(s) \,|\, Zn^{2+}(1\ M) \,\|\, H^+(1\ M) \,|\, H_2(1\ atm) \,|\, Pt(s)$$

Anode (oxidation): $Zn(s) \longrightarrow Zn^{2+}(aq)(1\ M) + 2e^-$

Cathode (reduction): $2H^+(aq)(1\ M) + 2e^- \longrightarrow H_2(g)(1\ atm)$

Overall: $Zn(s) + 2H^+(aq)(1\ M) \longrightarrow Zn^{2+}(aq)(1\ M) + H_2(g)(1\ atm)$
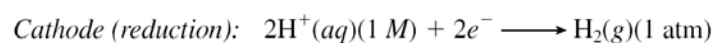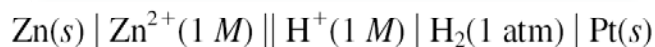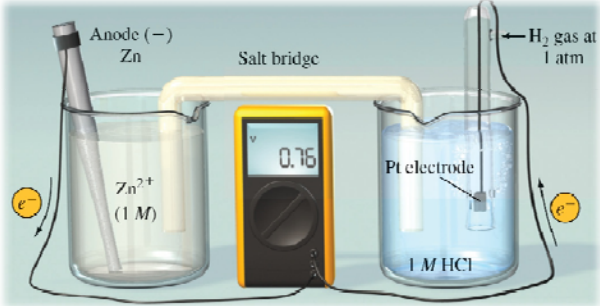
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Measuring $E^o_{Zn^{2+}/Zn}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

The standard reduction potential of zinc is − 0.76 V.

The standard reduction potential of zinc is negative, which means, when connected with hydrogen half cell, zinc tends to be oxidized, not reduced.

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Measuring $E^o_{Cu^{2+}/Cu}$

standard reduction potential for copper

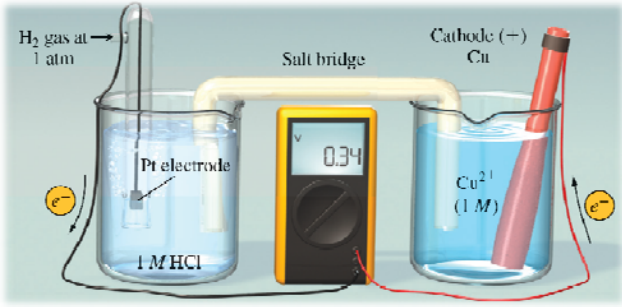$$Pt(s) \mid H_2(1\ atm) \mid H^+(1\ M) \parallel Cu^{2+}(1\ M) \mid Cu(s)$$

Anode (oxidation): $H_2(g)(1\ atm) \longrightarrow 2H^+(aq)(1\ M) + 2e^-$
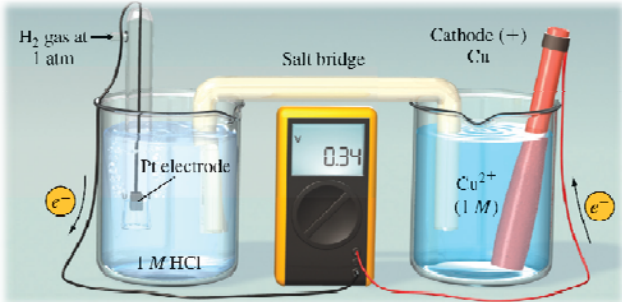
Cathode (reduction): $Cu^{2+}(aq)(1\ M) + 2e^- \longrightarrow Cu(s)$

Overall: $H_2(g)(1\ atm) + Cu^{2+}(aq)(1\ M) \longrightarrow 2H^+(aq)(1\ M) + Cu(s)$

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Measuring $E^{o}_{Cu^{2+}/Cu}$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$E^{o}_{cell} = E^{o}_{Cu^{2+}/Cu} - E^{o}_{H^{+}/H_2}$$

The standard reduction potential of copper is + 0.34 V.

$$0.34 \text{ V} = E^{o}_{Cu^{2+}/Cu} - 0 \text{ V}$$

$$E^{o}_{Cu^{2+}/Cu} = 0.34 \text{ V}$$

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Comparison of $E°$ Values

Cu^{2+} (aq) + 2e$^-$ → Cu (s) $E° = + 0.34$ V

Cathode   2H$^+$ (aq) + 2e$^-$ → H$_2$ (g) $E° = 0$ V

Anode   Zn^{2+} (aq) + 2e$^-$ → Zn (s) $E° = - 0.76$ V

Easier to be reduced ↑

Easier to be oxidized ↓

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E^{o}_{Cell} of a Zinc-Copper Cell

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$
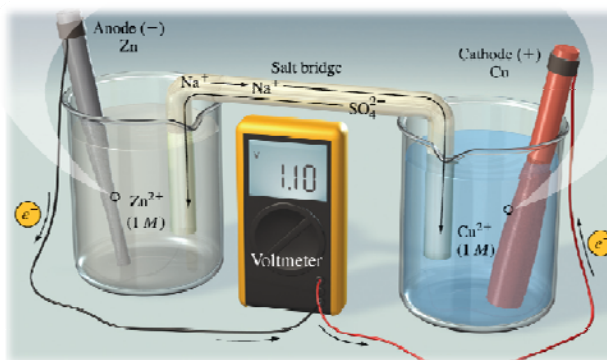
$$E^{o}_{cell} = E^{o}_{Cu^{2+}/Cu} - E^{o}_{Zn^{2+}/Zn} = 0.34V - (-0.76V)$$

$$E^{o}_{cell} = 1.10 \text{ V}$$

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Standard reduction potentials (E^{o}) of some half-reactions at 25°C   19.3

Increasing ease of reduction
Increasing strength as an oxidizing agent

Increasing ease of oxidation
Increasing strength as a reducing agent

Half-reaction	E^{o}
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18

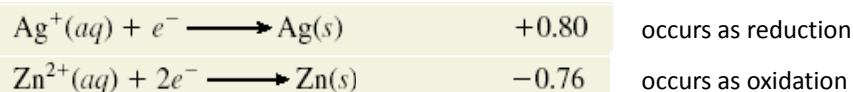*Dr. Al-Saadi*   24

Calculating the Standard Cell Potential (E^{o}_{cell})

- Example:

Calculate the standard cell potential of the following cell:

Zn(s) | Zn²⁺(1 *M*) || Ag⁺(1 *M*) | Ag(s)

From the table of standard reduction potentials:

$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0.80	occurs as reduction
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	−0.76	occurs as oxidation

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$$

$$E^{o}_{cell} = E^{o}_{Ag^{+}/Ag} - E^{o}_{Zn^{2+}/Zn} = 0.80V - (-0.76V)$$

$$E^{o}_{cell} = 1.56\ V$$

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Calculating the Standard Cell Potential (E^{o}_{cell})

- Example:

Write the balanced equation of the overall cell reaction.

Zn(s) | Zn²⁺(1 *M*) || Ag⁺(1 *M*) | Ag(s)

$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$	+0.80	occurs as reduction
$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$	−0.76	occurs as oxidation

$2\,Ag^{+}\,(aq) + 2\,e^{-} \rightarrow 2\,Ag\,(s)$

$Zn\,(s) \quad \rightarrow 2e^{-} + Zn^{2+}\,(aq)$

$Zn\,(s) + 2Ag^{+}\,(aq) \rightarrow Zn^{2+}\,(aq) + 2Ag\,(s)$
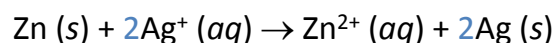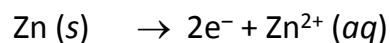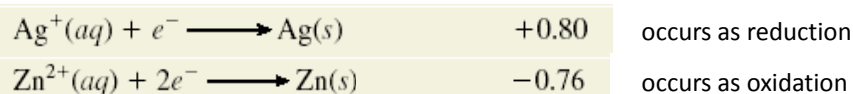
Standard reduction potential is an ***intensive property*** (like temperature and density), and it is not an extensive property (like mass and volume).

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Predicting the Occurrence of Redox Reactions

■ Example:

Determine what redox reaction, if any, occurs at 25°C when lead metal (Pb) is added to:

(a) 1.0 M solution of $NiCl_2$.

The proposed reaction is:

$$Pb(s) \;+\; Ni^{2+}(aq) \;\rightarrow\; Pb^{2+}(aq) \;+\; Ni\,(s)$$

oxidized   reduced

The proposed reaction will occur only if $E^o_{Ni^{2+}/Ni} > E^o_{Pb^{2+}/Pb}$

$$E^o_{Ni^{2+}/Ni} = -0.25\,V$$

Thus, the redox reaction will NOT occur.

$$E^o_{Pb^{2+}/Pb} = -0.13\,V$$

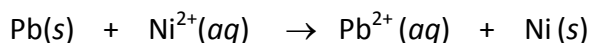*Dr. Al-Saadi*   27

Predicting the Occurrence of Redox Reactions

■ Example:

Determine what redox reaction, if any, occurs at 25°C when lead metal (Pb) is added to:

(b) 1.0 M solution of HCl.

The proposed reaction is:

$$Pb(s) \;+\; 2H^+(aq) \;\rightarrow\; Pb^{2+}(aq) + H_2(g)$$
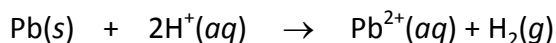
oxidized   reduced

The proposed reaction will occur only if $E^o_{H^+/H_2} > E^o_{Pb^{2+}/Pb}$

$$E^o_{H^+/H_2} = 0.00\,V$$

Thus, the redox reaction will occur

$$E^o_{Pb^{2+}/Pb} = -0.13\,V$$

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Relationship between E^{o}_{cell} and ΔG^{o}

- Is there a relationship between **thermodynamics** and **electrochemistry**?

- In a galvanic cell, *chemical (potential) energy* is converted to *electric energy*.

  electric energy = (total electric charge) × (cell potential)

  | Joules | = | Coulombs | × | Volts |

- Since $w_{max} = -w_{electrical} = -nFE_{cell}$

  and $w_{max} = \Delta G$

  then: $\Delta G = -nFE_{cell}$

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Relationship between E^{o}_{cell} and ΔG^{o}

- For reactants and products at their standard states:

  $$\Delta G^{o} = -nFE^{o}_{cell}$$

  ΔG^{o} : Standard free energy change

  n: Number of moles of electrons that pass through the circuit.

  F: Faraday's constant (the electric charge contained in 1 mol of electrons) $1\ F = 9.65 \times 10^4$ J / V · mol e⁻

  E^{o}_{cell} : Standard cell potential.

  - When ΔG^{o} is –ve , the value of E^{o}_{cell} is +ve.
    (the process is **spontaneous**).
  - When ΔG^{o} is +ve , the value of E^{o}_{cell} is –ve.
    (the process is **nonspontaneous**).

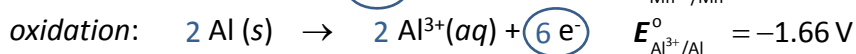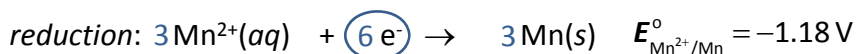*Dr. Al-Saadi*   30

19.4

Relationship between E°_{cell} and ΔG°

- **Example:**
  Give the balanced equation and determine the standard free energy change for the following reaction at 25°C :

  $$2 \text{ Al } (s) + 3 \text{ Mn}^{2+}(aq) \rightarrow 2 \text{ Al}^{3+}(aq) + 3 \text{ Mn } (s)$$

  The half-cell reactions:

  reduction: $3 \text{ Mn}^{2+}(aq) + 6 \text{ e}^- \rightarrow 3 \text{ Mn}(s)$ $E^{\circ}_{\text{Mn}^{2+}/\text{Mn}} = -1.18 \text{ V}$

  oxidation: $2 \text{ Al } (s) \rightarrow 2 \text{ Al}^{3+}(aq) + 6 \text{ e}^-$ $E^{\circ}_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$

  $\Delta G^{\circ} = - nFE^{\circ}_{\text{cell}}$

  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -1.18 \text{ V} - (-1.66 \text{ V}) = +0.48$

  $\Delta G^{\circ} = - nFE^{\circ}_{\text{cell}} = -(6 \text{ e}^-)(9.65 \times 10^4 \text{ J/V·mol e}^-)(0.48 \text{ V})$

  $\qquad = -2.78 \times 10^5 \text{ J/mol} = -2.78 \times 10^2 \text{ kJ/mol}$

  (spontaneous)

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Relationship between E°_{cell} and K_c

$\Delta G^{\circ} = - RT \ln K$ ← (from Chapter 18)

$\Delta G^{\circ} = - nFE^{\circ}_{\text{cell}}$

Combining the above two equations:

$- RT \ln K = - nFE^{\circ}_{\text{cell}}$

Solving for E°_{cell} :

$$E^{\circ}_{\text{cell}} = \frac{RT}{nF} \ln K$$

At 25°C:

$$E^{\circ}_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \ln K = \frac{0.0592 \text{ V}}{n} \log K$$

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Relationship between E°_{cell} and K_c

- Example:

  Calculate the equilibrium constant for the following reaction at 25°C :

  $$2\,Al\,(s) + 3\,Mn^{2+}(aq) \rightarrow \quad 2\,Al^{3+}(aq) + \; 3\,Mn\,(s)$$

  $$E^{\circ}_{cell} = \frac{0.0257 \;\; V}{n} \ln K$$

  $$K = e^{\frac{nE^{\circ}_{cell}}{0.0257\,V}}$$

  $$K = e^{\frac{(6)(0.48\,V)}{0.0257\,V}} = 4.7 \times 10^{48}$$

  Remember that the process is spontaneous (large K_c value)

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